

ALKYNYLRUTHENIUM DENDRIMERS: SYNTHESSES AND MULTIPHOTON ABSORPTION

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Introduction

Metal-containing dendrimers are attracting considerable current interest because the presence of the metal can imbue the dendrimer with specific electronic, magnetic, or optical properties. There have been several reports of π -delocalizable alkyneplatinum dendrimers, which contain metal atoms with 16 valence electrons,¹ but related 18 valence electron metal-containing dendrimers are comparatively little-explored. We have been studying the nonlinear optical (NLO) properties of metal alkyne complexes and noted enhancement of such properties in proceeding to metal complexes with 18 valence electrons.² As a consequence, we have targeted 18 valence electron alkyne ruthenium dendrimers, and have demonstrated their NLO efficiency, which can be increased on generational increase without loss of optical transparency.³ While NLO results for these dendrimers are promising, the long-winded syntheses mitigate against detailed studies. We report herein a more rapid route to alkyne ruthenium dendrimers, and selected studies of their NLO properties, emphasizing wavelength dependence studies and reversible switching of nonlinearity under electrochemical control.

Experimental

Syntheses. The dendrimers were synthesized from alkyne ruthenium complex precursor dendrons and cores following our communicated procedures or minor modifications thereof.⁴ A selected synthesis is shown in **Figure 1**.

Third-order nonlinearities. Z-scan measurements were performed using two amplified femtosecond laser systems. The first system was based on a Coherent Mira-900D Ti-sapphire oscillator and included a chirped pulse Ti-sapphire amplifier operating at a repetition rate of 30 Hz. This system was used at wavelength 800 nm and provided ca 150 fs FWHM pulses. The second system was a Clark-MXR CPA-2001 regenerative amplifier pumping a Light Conversion TOPAS optical parametric amplifier. This system was operated at a repetition rate of 250 Hz or 83 Hz (reduced from the usual default rate of 1 kHz to minimize potential problems with thermal effects and sample photodecomposition) in the range 525 nm to 1600 nm with pulse duration of ca 150 fs.

Results and Discussion

The periphery-metalated dendrimers were prepared as summarized in **Figure 1**.

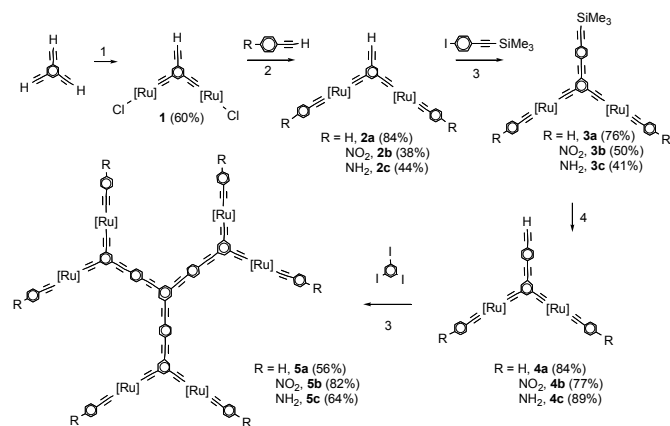


Figure 1. Syntheses of periphery-metalated dendrimers **5a-c**. [Ru] = *trans*-[Ru(dppe)₂]. (1) a. *cis*-[RuCl₂(dppe)₂], NH₄PF₆; b. NEt₃; (2) NH₄PF₆, NEt₃; (3) Pd(PPh₃)₄, NEt₃; (4) Bu₄NF.

The synthesis of **1** proceeds by “steric control” to afford a dimetalated dendron – the bulky ligated ruthenium centers shield the remaining terminal ethynyl group in **1** from attack by further ruthenium reagent. The ruthenium centers react with various arylacetylenes to give **2a-c**, and then the terminal ethynyl group can be reacted with 4-iodo(trimethylsilyl)ethynyl)benzene under Sonogashira conditions to afford **3a-c**. Removal of the trimethylsilyl protecting groups gives **4a-c**, which can be coupled with 1,3,5-triiodobenzene to afford **5a-c**.

The core-metalated dendrimer is depicted in **Figure 2**, and the dendrimers metalated at the core and periphery are shown in **Figure 3**.

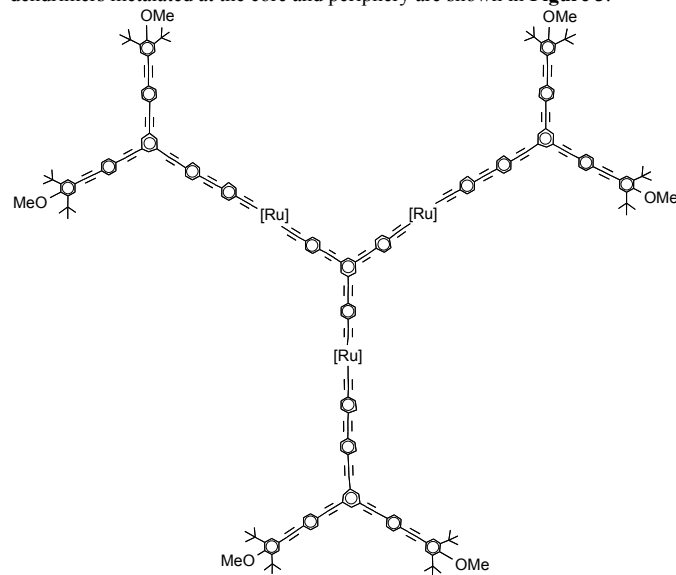


Figure 2. Core-metalated dendrimer **6**.

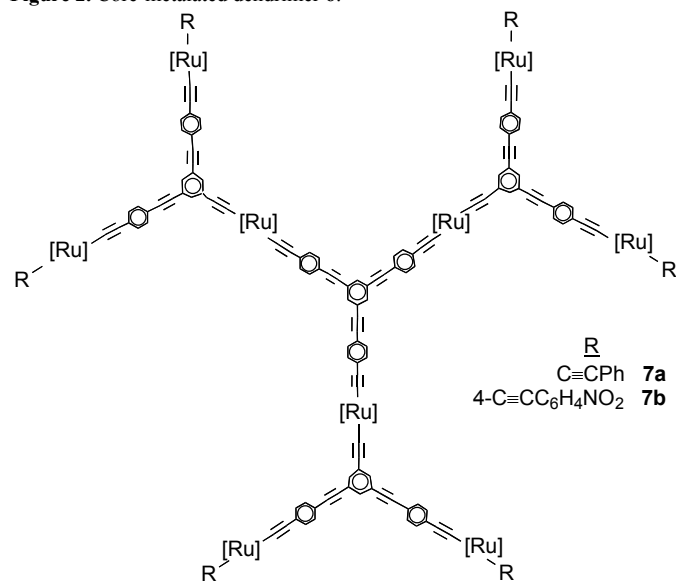


Figure 3. Core- and periphery-metalated dendrimers **7a,b**.

The spectral dependence of the cubic nonlinearity of **5b**,^{4(b)} **7b**,⁵ and **7a** have been determined and are shown in **Figure 4**, **Figure 5**, and **Figure 6**, respectively, the first such studies for inorganic complexes. The wavelength dependence of **5b** has been modeled assuming that resonances with the two transitions seen in the linear optical spectrum are relevant for the NLO properties. The cubic nonlinearity can be understood in terms of a competition between two-photon absorption and absorption saturation.

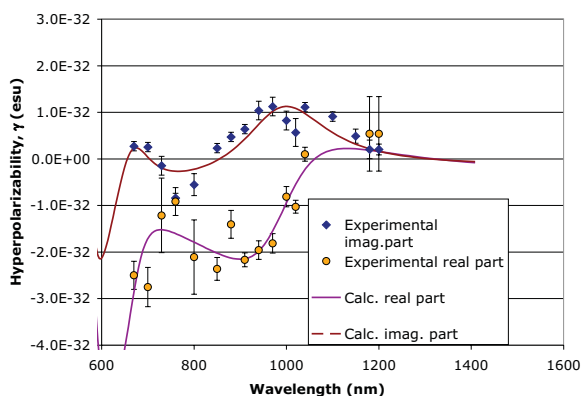


Figure 4. Experimental and calculated values of γ_{real} and γ_{imag} for **5b**.

The wavelength dependence of the cubic nonlinearity of **7b** reveals two-photon absorption at ca 750 nm and efficient three-photon absorption (a type of fifth-order nonlinearity) at ca 1200 nm. Dendrimer **7a** exhibits two-photon absorption in the short wavelength region, but is not a significant three-photon absorber at long wavelength. Further studies to understand this differing behavior seen upon dendrimer structural modification are currently underway.

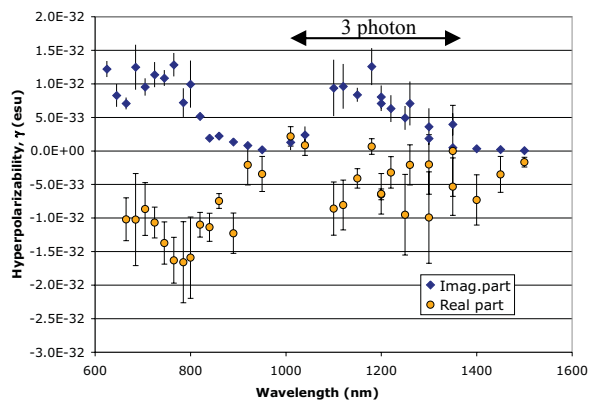


Figure 5. Experimental values of the effective values of γ_{real} (open circles) and γ_{imag} (filled blue squares) for **7b** at light intensities of ca 100 GW cm^{-2} .

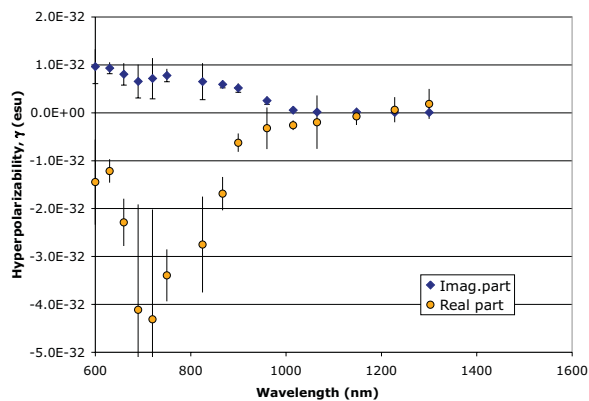


Figure 6. Experimental values of γ_{real} and γ_{imag} for **7a** at light intensities of ca 100 GW cm^{-2} .

These organometallic complexes can be reversibly oxidized under electrochemical control, and the change in oxidation state is accompanied by changes in linear and nonlinear optical properties. For specific dendrimers, this can correspond to a change in sign for both refractive and absorptive nonlinearity, i.e. electrochemical switching of molecular cubic nonlinearity.^{3(d),6}

Conclusions

Ruthenium alkynyl dendrimers are accessible in a facile fashion by employing “steric control” to prepare the necessary metal-containing dendrons. Preliminary studies of the wavelength dependence of cubic nonlinearity in these complexes has revealed fifth-order NLO behavior for one example. Reversible redox processes in these dendrimers have been used to “switch” cubic nonlinearity.

Acknowledgements. We thank the Australian Research Council for support of this work and Johnson-Matthey Technology Centre for the generous loan of ruthenium salts. MGH is an ARC Australian Professorial Fellow.

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